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STUDIES OF INSECTICIDE RESIDUES ON GRAPES AND IN WINES

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Insecticides applied to grapes may occur in such form and quantity in residues on harvested fruit and persist through the processing procedure to such an extent as to be objectionable in wines. Factors affecting the amount of insecticide residues at harvest include spray concentration and rate of application, joint or subsequent use of other insecticides, fungicides, and stickers, time of last application in relation to harvest, and rainfall (Fahey and Still 3).<sup>1/</sup>

Since a considerable part of the grape crop in northern Ohio is used in making wines, cooperative studies<sup>2/</sup> were undertaken to determine whether residues of lead, arsenic, DDT, parathion, EPN, and methoxychlor persist in deleterious amounts to contaminate the finished product.

Concord and Catawba grapes from the experimental plots of the Entomology Research Division at Sandusky, Ohio, were processed, and the wine was made at commercial wineries using their regular equipment. Only small lots of wine were made, not exceeding 30 gallons in any one lot, using either 30-gallon oak barrels or 13-gallon glass carboys.

The wine was made by two processes. The pulp-ferment process consisted of crushing the grapes without removing the stems, adding sugar, and fermenting this mash in an open vat. The fermented pulp, or mash, was then pressed and the wine placed in a wooden cask or glass carboy for further fermentation. The cold-press process consisted of crushing and pressing the grapes without removing the stems. Sugar was added to the fresh juice, which was then placed in a wooden cask or glass carboy and fermented.

Ameliorated wines were those to which both sugar and water were added before fermentation, as per specifications of the U.S. Bureau of Internal Revenue.

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<sup>1/</sup> Numbers in parentheses refer to Literature Cited at the end of this report.

<sup>2/</sup> Mantey Vineyards, Venice, Ohio, Limpert Winery, Westlake, Ohio, and Meier's Wine Cellars, Inc., Sandusky, Ohio, processed the grapes into wine. The Horticultural Department, Ohio Agricultural Experiment Station, Wooster, analyzed some of the samples for DDT residues. Most residue analyses were performed by the Pesticide Chemicals Research Branch, Entomology Research Division.

## METHODS OF ANALYSIS

Samples of ripe grapes were frozen as soon as possible after collecting and held in this condition until analyzed. Residues of organic insecticides were recovered from the fruit surface by stripping the grapes with benzene and from the juice and wine samples by extraction with benzene. After shaking the solvent for 30 minutes, it was decanted into a sample storage bottle and dried over sodium sulfate. An aliquot was taken for analysis.

For DDT and methoxychlor, redistilled benzene was the solvent. DDT was determined by either the Schechter-Haller (6) or Stiff-Castillo method (7) and methoxychlor by the Fairing and Warrington method (4). Lead arsenic residues were wet ashed with sulfuric and nitric acids. Lead residues were determined by electrolytic precipitation and titration (Wichmann, et al. 8) and arsenic by bromate titration of arsenic trichloride (Jones 5, and Association of Official Agricultural Chemists 1). Parathion and EPN were extracted with benzene and determined by the colorimetric method of Averell and Norris (2).

### LEAD AND ARSENIC RESIDUES

It is well known that applications of three or more sprays of lead arsenate after bloom may result in excessive residues of lead and arsenic on the grapes at harvest. Whether the samples analyzed include only the berries or entire clusters, including the stems, the amounts of residues do not vary much. The level and range of lead and arsenic residues resulting from standard lead arsenate-spray programs on fresh grapes are shown in table 1. A summary of lead and arsenic residues in the successive stages of wine processing of grapes from plots receiving the above treatments is given in table 2. In the analysis of the residues on fruits, the grape berries were used without stems. Both stems and berries were used in the processing of the wines.

Table 1.—Level and range of lead arsenic residues on fresh grapes at harvest following use of standard lead arsenate-spray schedules

Year	Postbloom applications of lead arsenate (3 lbs. per 100 gal.) on—	Date of harvest	Residues (p.p.m.)	
			Pb	As <sub>2</sub> O <sub>3</sub>
1942---	June 11 and 30, July 17-----	Sept. 16	35.4	12.3
1943---	June 24, July 1 and 25, Aug. 2-----	Oct. 2	18.0	8.1
1944---	June 16 and 28, July 5 (plus two cover sprays of bordeaux-oil)	Oct. 23	20.3	9.1
1945---	June 24, July 3 and 20 (plus two cover sprays of bordeaux-oil)	Oct. 9	16.9	8.4

Table 2.--Amount of lead and arsenic residues in wine processed from Concord grapes sprayed with lead arsenate 1/

Stage of Processing	Residues (p.p.m.) for indicated year and process											
	1942			1943			1944			1945		
	Cold press			Cold press : Pulp ferment			Cold press : Cold press : Ameliorated:ameliorated			Average (all lots)		
	Pb	As <sub>2</sub> O <sub>3</sub>		Pb	As <sub>2</sub> O <sub>3</sub>		Pb	As <sub>2</sub> O <sub>3</sub>		Pb	As <sub>2</sub> O <sub>3</sub>	
Berries	35.4	12.3	18.0	8.1	18.0	8.1	20.3	9.1	16.9	8.4	21.7	9.3
Pulp with stems	--	--	--	--	15.0	9.0	--	--	--	--	--	--
Juice:												
Fresh	11.9	5.5	6.0	3.4	--	--	--	--	5.5	3.6	6.8	4.2
Ameliorated	--	--	--	--	--	--	4.5	4.0	--	--	--	--
After ferment	--	--	--	--	6.0	5.1	--	--	--	--	--	--
Pomace:												
Fresh	200.0	54.9	80.0	19.6	--	--	--	--	--	--	--	--
After ferment	--	--	--	--	80.0	16.9	--	--	--	--	--	--
Wine	--	--	3.6	1.5	4.9	2.2	.7	1.4	.8	1.4	--	--
Lees	--	--	--	--	--	--	29.9	14.1	17.1	13.1	--	--
Filtered	.4	4.4	1.0	1.8	3.6	2.7	1.0	1.8	1.0	1.2	1.4	2.3
In cask bottom	128.0	37.5	90.0	37.1	28.2	47.9	1.0	1.9	.8	1.2	--	--

1/ Grapes from plots treated as shown in table 1.



The data in tables 1 and 2 show that 69 percent of the lead (Pb) and 55 percent of the As<sub>2</sub>O<sub>3</sub> residues on the fresh berries were lost in processing the berries into juice, 79 and 45 percent of the remaining residues were lost, respectively, in processing the juice into wine, for a total loss of 93 percent of the lead and 75 percent of the As<sub>2</sub>O<sub>3</sub> in the complete processing procedure. Since analyses of lead residues are not accurate below 0.4 p.p.m., the amounts reported may be high. However, the amounts of lead and arsenic did not exceed the tolerance for those materials in the finished wine.

#### DDT RESIDUES

In 1944 grapes sprayed with  $1\frac{1}{2}$  pounds of 50-percent DDT wettable powder per 100 gallons of water on June 16 and 24, July 16, and August 1 and harvested on September 22 were fermented in the pulp, ameliorated with sugar and water, and processed into wine. The DDT residue on the fresh berries was not determined. On December 5, 1944, an unfiltered composite of the 22 gallons of wine in the original cask contained 0.4 p.p.m. of DDT and a composite of the sediment in the lower 5 inches of the cask contained 0.2 p.p.m. of DDT. The bulk of the wine was then transferred to a 15-gallon cask. On June 12, 1945, a composite of the unfiltered wine still contained 0.4 p.p.m. of DDT and the sediment in the lower 5 inches of the cask had 0.2 p.p.m. A composite of the wine filtered twice contained only 0.2 p.p.m. of DDT.

In 1946 Concord and Catawba grapes sprayed with  $1\frac{1}{2}$  pounds of ferbam per 100 gallons of water on April 24 and with  $1\frac{1}{2}$  pounds of 50-percent DDT wettable powder and  $1\frac{1}{2}$  pounds of ferbam per 100 gallons of water on June 8 (prebloom) and 27, July 5 and 15, and August 7 and 26 and harvested on September 30 and October 10, respectively, were processed into wine. The Concord grapes were fermented in the pulp and then pressed for wine processing. The Catawba grapes were cold pressed for wine processing. In both methods the juice was ameliorated with sugar and water.

In 1947 Catawba grapes sprayed with  $1\frac{1}{2}$  pounds of 50-percent DDT wettable powder with fungicide and sticker per 100 gallons of water on July 7 and 29, August 4 and 25, September 11, and October 6 were harvested on October 16 and made into wine by the cold-press method and the juice was ameliorated with sugar and water. As a check, Catawba grapes sprayed only with 2 pounds of 50-percent DDT wettable powder per 100 gallons on July 21 were processed into wine in a similar manner at the same time.

In 1950 Concord grapes sprayed with  $1\frac{1}{2}$  pounds of 50-percent DDT wettable powder per 100 gallons of water on June 23 and July 3 with a sticking agent and on August 15 and 30 without a sticking agent were harvested on October 7 and made into wine by the cold-press method. The DDT residues in the wine processed in 1946, 1947, and 1950 are given in table 3.

Table 3.—Amount of DDT residues in wine processed from grapes sprayed with DDT and ferbam

Stage of processing	Residues (p.p.m.) for indicated year, variety, process, and number of sprays				
	1946	1946	1947	1950	
	Concord,	Catawba,	Catawba, cold press:	Concord,	
	pulp fer-	cold press:		cold press,	
	ment, 6	6 sprays		4 sprays	
	sprays		6 sprays; 1 spray		
Berries (no stems)-----	5.1	13.3	29.12	0	2.7
Fresh juice-----	0	0	0	0	.1
Fresh pomace-----	51.0	45.4	--	--	17.5
First rack:					
Wine-----	1.0	1.2	0	0	0
Lees-----	1.2	1.4	--		--
Final rack:					
Unfiltered wine-----	0	0	--	--	--
Filtered wine-----	0	0	--	--	--
Lees-----	0	0	--	--	--

The data show that the DDT residue on grapes, regardless of the amount, was eliminated in the wine-making process or reduced to well below the tolerance for DDT in the finished wine.

#### PARATHION, EPN, AND METHOXYCHLOR RESIDUES

In 1949 Catawba grapes sprayed with 4 ounces of actual parathion per 100 gallons of water on June 10 and 22, July 18 and 28, and August 25 or on the foregoing dates and on September 16 and harvested on October 2 were made into wine by the cold-press method and ameliorated with sugar.

In 1950 Concord grapes sprayed with 15-percent parathion, 25-percent EPN, or 50-percent methoxychlor wettable powders at 2 pounds per 100 gallons of water with a sticking agent on June 23 and July 3 and without a sticking agent on August 15 and 30 were harvested on October 7 and processed into wine by the cold-press method and ameliorated with sugar.

Residue data in table 4 show that neither EPN nor methoxychlor residues occurred in the finished wine. Parathion residues occurred in little more than a trace amount or not at all, even when more than the normal number of applications were made, the last near harvest.

Table 4.—Amount of residues in wine processed (cold press) from grapes sprayed with parathion, EPN, and methoxychlor

Stage of Processing	Residues (p.p.m.) from indicated insecticide applications					
	Parathion			EPN	Methoxychlor	
	6 sprays	7 sprays	4 sprays	4 sprays	4 sprays	
	1949		1950	1950		
Berries-----	0.15	0.39	<0.1	0.3	3.6	
Fresh juice:						
No sugar-----	0	0	--	--	--	
Sugar added---	0	0	<.1	.1	.4	
Fresh pomace--	.14	.84	.5	2.5	2.6	
	February 1950		January 1951			
First rack:						
Wine-----	0	0	<.05	0	0	
Lees-----	0	0	--	--	--	
	July 1951					
Second rack:						
Wine-----	0	0	--	--	--	
Lees-----	0	0	--	--	--	

#### SUMMARY

Three applications of lead arsenate to grapes after bloom resulted in excessive residues of lead and  $\text{As}_2\text{O}_3$  on the grape berries at harvest. When grapes carrying excessive amounts of lead and  $\text{As}_2\text{O}_3$  were made into wine, practically all the lead residue and about three-fourths of the arsenic were lost during the wine-making process. Much of the lost residue was accounted for in the pomace and lees. Filtering the wine did not remove either lead or arsenic residues. Slightly less arsenic occurred in wine processed by the cold-press method than in wine processed by the pulp-ferment method. The amounts of lead and arsenic did not exceed the tolerance for those materials in the finished wine.

Tests conducted in 1946, 1947, and 1950 showed that DDT residues on fresh grapes were largely dissipated in the wine-making process, regardless of whether the wine was made by the pulp-ferment or cold-press method. Practically all the DDT was accounted for in the pomace.

Wine made from grapes sprayed excessively with parathion and close to harvest contained no parathion or little more than a trace. These and similar results with grapes sprayed excessively with DDT indicate that residues of organic insecticides on grapes are unlikely to occur in the finished wine. Similar results were obtained in less extensive tests with grapes sprayed with EPN and methoxychlor.



## LITERATURE CITED

- (1) Association of Official Agricultural Chemists.  
1933. Change in the official and tentative methods of analysis made at the forty-eighth annual convention, October 31, November 1 and 2, 1932. XXIX. Metals in foods. Assoc. Off. Agr. Chem. Jour. 16: 68-85.
- (2) Averell, P. R., and Norris, M. V.  
1948. Estimation of small amounts of O,O-diethyl O,p-nitrophenyl thiophosphate. Analyt. Chem. 20: 753-756.
- (3) Fahey, J. E., and Still, G. W.  
1961. Insecticide residues on grapes treated for control of insects. U.S. Dept. of Agr. ARS-33-66, 17 pp.
- (4) Fairing, J. D., and Warrington, H. P.  
1950. Colorimetric determination of small quantities of 1,1,1-trichloro-2,2-bis(p-methoxyphenyl)-ethane. Advn. Chem. Ser. 1: 260-265.
- (5) Jones, W. C.  
1934. Report on bromate methods for determination of arsenic in foods. Assoc. Off. Agr. Chem. Jour. 17: 202-204.
- (6) Schechter, M. S., and Haller, H. L.  
1944. Colorimetric tests for DDT and related compounds. Amer. Chem. Soc. Jour. 66: 2129-2130.
- (7) Stiff, H. A., and Castillo, J. C.  
1945. A colorimetric method for the micro-determination of 2,2-bis(p-chlorophenyl) 1,1,1-trichloroethane (DDT). Science 101: 440-443.
- (8) Wichmann, H. J., Murray, C. W., Harris, M., and others.  
1934. Methods for determination of lead in foods. Assoc. Off. Agr. Chem. Jour. 17: 108-135.

